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71	FULL NAME(S) OF APPLICANT(S)
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SASOL TECHNOLOGY (PROPRIETARY) LIMITED

72	FULL NAME(S) OF INVENTOR(S)
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VAN BERGE, Peter Jacobus
VAN DE LOOSDRECHT, Jan
BARRADAS, Sean

54	TITLE OF INVENTION
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"PRODUCTION OF FISCHER-TROPSCH SYNTHESIS PRODUCED WAX"

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THIS INVENTION relates to the production of Fischer-Tropsch synthesis produced wax. It relates in particular to a process for producing a clean wax product.

10 It is known from the prior art that clean wax products, ie wax products containing less than 50 mass ppm total cobalt, can be obtained during slurry phase Fischer-Tropsch synthesis involving contacting a synthesis gas comprising hydrogen and carbon monoxide at elevated temperature and pressure with a particulate supported cobalt Fischer-Tropsch synthesis catalyst, to produce the
15 clean wax products. The clean wax product can be defined as being the filtrate of the liquid Fischer-Tropsch synthesis product (ie reactor wax) continuously extracted directly from the reactor slurry phase through an in-situ primary filtration process. The particulate supported cobalt slurry phase Fischer-Tropsch catalysts are sufficiently strong so that little break-up thereof during extended
20 slurry phase Fischer-Tropsch synthesis runs takes place, and cobalt crystallites are sufficiently anchored to the catalyst support to prevent cobalt from readily dislodging and washing out of the cobalt catalyst during such extended slurry phase Fischer-Tropsch synthesis runs conducted at realistic conditions, also implying catalyst stability in the associated hydrothermal environment.

25 This objective is successfully achieved in the prior art through the introduction, during production of a catalyst precursor from which the catalyst is obtained, of additional processing step(s) to modify an already pre-shaped catalyst support, such as Al_2O_3 , MgO or TiO_2 , thus producing a modified catalyst support, wherein the cobalt crystallites are sufficiently anchored to the
30 selected catalyst support to prevent cobalt from readily dislodging and washing

out of the resultant cobalt catalyst during the extended slurry phase Fischer-Tropsch synthesis runs. Such a catalyst is preferably prepared through the aqueous phase impregnation of the modified catalyst support with cobalt.

- 5 However, the known slurry phase Fischer-Tropsch synthesis processes involving the use of the cobalt slurry phase Fischer-Tropsch catalysts hereinbefore described, suffer from the drawback that additional processing steps are required to modify the already pre-shaped catalyst supports. It is hence an object of this invention to provide a process for producing a clean wax product,
10 ie a wax product having less than 50 mass ppm total cobalt, whereby this drawback is eliminated or at least reduced.

Thus, according to the invention, there is provided a process for producing a clean wax product, which process includes contacting, at an elevated
15 temperature between 180°C and 250°C and an elevated pressure between 10 bar and 40 bar, a synthesis gas comprising hydrogen and carbon monoxide with a cobalt slurry phase Fischer-Tropsch synthesis catalyst produced from a successful catalyst support, in a slurry phase Fischer-Tropsch synthesis reaction, to produce a clean wax product containing less than 50 mass ppm submicron
20 particulates of cobalt.

In this specification, a 'successful catalyst support' is defined as a catalyst support obtained from a catalyst support preparation step into which is integrated a catalyst support modification step and a pre-shaping step, ie the
25 catalyst support modification step and the catalyst pre-shaping step both take place during preparation of the catalyst support. In other words, the catalyst support modification is not effected as a separate step after the preparation of the catalyst support has been completed.

30 In the preparation of the successful catalyst support, a modifying component Me, where Me is any element of the Periodic Table that increases the inertness

of the catalyst support towards dissolution in an aqueous environment during cobalt impregnation or hydrothermal attack during Fischer-Tropsch synthesis, is introduced onto the catalyst support, followed by calcination of the thus modified catalyst support. The cobalt slurry phase Fischer-Tropsch catalyst is then produced from the successful catalyst support by impregnating the
5 successful catalyst support with an aqueous solution of a cobalt salt, to form an impregnated support; partially drying the impregnated support; calcining the partially dried impregnated support, to obtain a catalyst precursor; and reducing the catalyst precursor to form the cobalt slurry phase Fischer-Tropsch catalyst.

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The modifying component, Me, is preferably selected from Si, Ti, Cu, Zn, Ba, Co, Ni, Na, K, Ca, Sn, Cr, Fe, Li, Tl, Sr, Ga, Sb, V, Hf, Th, Ce, Ge, U, Nb, Ta, W, La and mixtures thereof.

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The modifying component, Me, that is present in the successful catalyst support thus serves to render the catalyst support, eg Al_2O_3 , TiO_2 , MgO or ZnO , which is normally partially soluble in an acid aqueous solution and/or in a neutral aqueous solution, less soluble or more inert in the acid aqueous solution and/or in the
20 neutral aqueous solution.

The introduction of the modifying component, Me, onto the catalyst support may be effected by incorporating the modifying component into a precursor of the catalyst support. This may include contacting a precursor of the modifying
25 component, Me, with the catalyst support precursor, for example, by means of doping, co-gelling or precipitation. The modifying component precursor may be a salt or an alkoxide of the modifying element.

In one embodiment of the invention, the successful catalyst support may be prepared in accordance with the process for manufacture of alumina silicates as
30 described in DE 3839580, which is hence incorporated herein by reference.

Thus, it may be prepared by hydrolyzing an aluminium alkoxide, obtained from the alkoxide process (e.g. Ziegler ALFOL process or the Condea "on-purpose" propriety process (German patent: DE 3244972, 1984)) at 90 °C. Thereafter, a dilute solution of orthosilicic acid may be added to the stirred mixture. This slurry can then be spray dried at 300 °C to 600 °C to obtain the trademark product: Siral, which can be tailored through calcination, to obtain the trademark product: Siralox, ie Sasol Germany GmbH proprietary materials.

In another embodiment of the invention, the precursor of the modifying component may be an inorganic cobalt compound so that the modifying component is cobalt (Co). The inorganic cobalt precursor, when used, may be a cobalt salt (eg $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) which can be mixed into the slurry (e.g. boehmite slurry obtained from the alkoxide process), gelled by the addition of nitric acid and spray dried.

The modified catalyst support may then be calcined at a temperature of from 400°C to 900°C, preferably from 600°C to 800°C, and for a period of from 1 minute to 12 hours, preferably from 1 hour to 4 hours.

The method of forming the catalyst precursor may be in accordance with that described in US 5,733,839, WO 99/42214, and/or WO 00/20116, which are thus incorporated herein by reference. Thus, the impregnation of the successful catalyst support with the active catalyst component, ie the cobalt, or its precursor aqueous solution, may comprise subjecting a slurry of the catalyst support, water and the active catalyst component or its precursor to a sub-atmospheric pressure environment, drying the resultant impregnated carrier under a sub-atmospheric pressure environment, and calcining the dried impregnated carrier, to obtain the catalyst precursor.

If a higher catalyst cobalt loading is required, then a second or even a third impregnation, drying, and calcination step may thereafter be carried out after the first impregnation, drying, and calcination step hereinbefore described.

5 During the slurry phase cobalt impregnation step(s), a water soluble precursor salt of Pt or Pd, or mixtures of such salts, may be added, as a dopant capable of enhancing the reducibility of the active component. The mass proportion of this dopant, when used, to cobalt may be between 0.01:100 and 0.3:100.

10 The process may include subjecting the wax product that is produced, to primary separation to separate the wax product from the catalyst. A serious problem that may arise when utilizing a cobalt slurry phase Fischer-Tropsch catalyst, not being a cobalt slurry phase Fischer-Tropsch catalyst prepared according to the invention, as observed during larger scale pilot plant slurry
15 phase Fischer-Tropsch synthesis runs, is the undesired high cobalt content of the wax product. Typically, the wax product may contain cobalt contamination levels in excess of 50 mass ppm, even after secondary ex-situ filtration through a Whatman no. 42 (trademark) filter paper (the product of such filtration is hereinafter referred to as 'secondary filtered reactor wax'). Due to the high cost
20 of cobalt, this is a highly undesirable problem which has thus been solved, or at least alleviated, with this invention. The said Al_2O_3 , TiO_2 , MgO or ZnO based catalyst supports are thus modified and pre-shaped during the catalyst support preparation step, a process that may include spray-drying and calcination, in order to increase inertness of the catalyst support in an aqueous (neutral or
25 acidic) environment during the cobalt nitrate impregnation step, and thus prevent the formation of cobalt-rich ultra fine particulates during slurry phase Fischer-Tropsch synthesis.

The invention will now be described in more detail with reference to the
30 following non-limiting examples and the accompanying drawings.

In the drawings

FIGURE 1 shows cumulative dissolution profiles of a pure pre-shaped alumina catalyst support (Puralox SCCa) and a silica modified catalyst support (Siralox 1.5 support), at a solids concentration of 2% (w/w); and

FIGURE 2 depicts the cobalt contamination level of secondary filtered wax product as a function of Fischer-Tropsch slurry phase synthesis time on stream, as observed on Pilot Plant scale. Cobalt supported Fischer-Tropsch synthesis catalysts were compared with catalysts supported as follows: (i) a pure pre-shaped alumina particulate catalyst support known by the trademark: Puralox SCCa, as supplied by SASOL Germany GmbH, (catalyst B), and (ii) a pre-shaped silica modified alumina catalyst support known by the trademark: Siralox 1.5, as supplied by SASOL Germany GmbH (catalyst A), which is in accordance with the invention.

In the example, two catalyst supports, and supported cobalt slurry phase Fischer-Tropsch synthesis catalysts obtained therefrom, are compared:

Puralox catalyst

support: This catalyst support is that obtainable under the trademark Puralox SCCa 2/150 from SASOL Germany GmbH of Überseering 40, 22297, Hamburg, Germany. It is a pure gamma-alumina support, and is prepared by calcination of boehmite ($\text{AlO}(\text{OH})$) at 750°C .

Siralox 1.5 catalyst

support: The successful catalyst support may be prepared by hydrolyzing an aluminium alkoxide, obtained from the alkoxide process (e.g. Ziegler ALFOL process or the Condea "on-purpose" proprietary process (German patent: DE 3244972, 1984)) at 90°C . Thereafter, a dilute solution of orthosilicic acid was added to the stirred mixture. This

slurry can then be spray dried at 300°C to 600°C to obtain the trademark product: Siral, which can be tailored through calcination, to obtain the trademark product: Siralox, ie Sasol Germany GmbH proprietary product. The silica content thereof is 1.5% (m/m).

EXAMPLE 1

1.1 Conductivity Measurements

Alumina dissolves in an aqueous medium at low pH. The dissolution of alumina results in the formation of aluminium ions. As more alumina dissolves, the concentration of aluminium ions increases with time. The increase of aluminium ions with time was monitored by measuring conductivity at a constant pH of 2. The pH was kept constant by automated addition of a 10% nitric acid solution. The results are set out in Figure 1.

In Figure 1, the cumulative mg Al dissolved per m² fresh catalyst support is plotted against time. It can be seen that the unprotected pure alumina (Puralox catalyst support) dissolves faster than the successful silica modified alumina (Siralox 1.5 catalyst support).

1.2 Catalyst preparation

Catalyst A

A supported cobalt catalyst precursor was prepared on the Siralox 1.5 successful catalyst support with a porosity of 0.46ml/g, as catalyst support material. A solution of 17.4kg of Co(NO₃)₂·6H₂O, 9.6g of (NH₃)₄Pt(NO₃)₂, and 11 kg of distilled water was mixed with 20.0kg of the Siralox 1.5 successful catalyst support, by adding the successful catalyst support to the solution. The slurry was added to a conical vacuum drier and continuously mixed. The temperature of this slurry was increased to

60°C after which a pressure of 20kPa (a) was applied. During the first 3 hours of the drying step which commenced when the pressure of 20kPa(a) was applied, the temperature was increased slowly and reached 95°C after the 3 hours. After the 3 hours the pressure was decreased to 3-15kPa(a), and a drying rate of 2.5m%/h at the point of incipient wetness was used. The complete impregnation and drying step took 9 hours, after which the impregnated and dried catalyst support was immediately and directly loaded into a fluidized bed calciner. The temperature of the dried impregnated catalyst support was about 75°C at the time of loading into the calciner. The loading took about 1 to 2 minutes, and the temperature inside the calciner remained at its set point of about 75°C. The impregnated and dried material was heated from 75°C to 250°C, using a heating rate of 0.5°C/min and an air space velocity of 1.0m³/kg Co(NO₃)₂.6H₂O/h, and kept at 250°C for 6 hours.

To obtain a catalyst with a cobalt loading of 30g Co/100g Al₂O₃, a second impregnation/drying/calcination step was performed. A solution of 9.4 kg of Co(NO₃)₂.6H₂O, 15.7g of (NH₃)₄Pt(NO₃)₂, and 15.1kg of distilled water was mixed with 20.0kg of the ex first impregnation and calcination intermediate material, by adding this material to the solution.

The slurry was added to a conical vacuum drier and continuously mixed. The temperature of this slurry was increased to 60°C after which a pressure of 20kPa(a) was applied. During the first 3 hours of the drying step, the temperature was increased slowly and reached 95°C after 3 hours. After 3 hours the pressure was decreased to 3-15kPa(a), and a drying rate of 2.5m%/h at the point of incipient wetness was used. The complete impregnation and drying step took 9 hours, after which the impregnated and dried intermediate material was immediately and directly loaded into the fluidized bed calciner. The temperature of the dried impregnated intermediate material was about 75°C at the time of loading into the calciner. The loading took about 1 to 2 minutes, and the

temperature inside the calciner remained at its set point of about 75°C. The impregnated and dried intermediate material was heated from 75°C to 250°C, using a heating rate of 0.5°C/min and an air space velocity of 1.0m³/kg Co(NO₃)₂·6H₂O/h, and kept at 250°C for 6 hours. The resultant 30g Co/100g Al₂O₃ catalyst was activated, ie reduced in a pure hydrogen environment in an atmospheric pressure fluidized bed at an elevated temperature of 425°C, to obtain the cobalt slurry phase Fischer-Tropsch synthesis catalyst (catalyst A).

Catalyst B

A supported cobalt catalyst precursor was prepared in a similar manner to that described for catalyst A, except that the catalyst precursor was prepared on the pure alumina pre-shaped support, Puralox SCCa 2/150. The resultant catalyst precursor was also reduced in a pure hydrogen environment in an atmospheric pressure fluidized bed at an elevated temperature of 425°C, to obtain the cobalt slurry phase Fischer-Tropsch synthesis catalyst (catalyst B).

1.3 Pilot Plant slurry phase Fischer-Tropsch synthesis test

During a confidential Pilot Plant slurry phase Fischer-Tropsch synthesis test run, using 5kg of the catalyst prepared on unmodified alumina, ie catalyst B, in a 1.1m high bubble column reactor with an external recycle, the secondary filtered reactor wax product turned grey after about 10 days on-line and the cobalt content increased to 350 mass ppm after 25 days on line, as shown in Figure 2. Pilot Plant scale Fischer-Tropsch synthesis test runs were performed under realistic conditions:

Reactor temperature: 230°C

Reactor pressure: 20 Bar

%(H₂ + CO) conversion: 50-70%

Feed gas composition:

H ₂ :	about ('ca') 50 vol%
CO:	ca 25 vol%
Balance:	Ar, N ₂ , CH ₄ and/or CO ₂

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A similar confidential Pilot Plant slurry phase Fischer-Tropsch synthesis test run was also performed on catalyst A, and showed a substantial improvement with respect to the submicron cobalt particulate contamination in the secondary filtered reactor wax product (Figure 2). After 38 days on stream, the cobalt contamination level of the secondary filtered reactor wax product was still within the specification of <50 mass ppm.

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From the Pilot Plant slurry phase Fischer-Tropsch synthesis tests, it can be seen that the improvement of the inertness of the alumina catalyst support by modifying it with silica, as shown by conductivity measurements, also prevented the formation of sub-micron cobalt rich particulates during slurry phase Fischer-Tropsch synthesis in the absence of catalyst break-up.

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1.4 Laboratory slurry phase Fischer-Tropsch synthesis

The cobalt catalyst precursors were reduced (as hereinbefore described) prior to Fischer-Tropsch synthesis in a tubular reactor at a hydrogen space velocity of 200ml hydrogen/(g catalyst.h) and atmospheric pressure. The temperature was increased to 425°C at 1°C/min, after which isothermal conditions were maintained for 16 hours.

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Between 10g and 30g of the resultant particulate catalyst, with the catalyst particles ranging from 38µm to 150µm, was suspended in 300ml molten wax and loaded in a CSTR with an internal volume of 500ml. The feed gas comprised hydrogen and carbon monoxide in a H₂/CO molar ratio

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of from 1.5/1 to 2.3/1. This reactor was electrically heated and sufficiently high stirrer speeds were employed so as to eliminate any gas-liquid mass transfer limitation. The feed flow was controlled by means of Brooks mass flow controllers, and space velocities ranging from 2 to $4\text{m}^3_n/(\text{kg}_{\text{cat}}\text{hr})$ were used. GC analyses of the permanent gases as well as the volatile overhead hydrocarbons were used in order to characterize the product spectra.

The catalysts, ie the reduced or activated precursors, were tested under realistic Fischer-Tropsch synthesis conditions:

Reactor temperature: 220 °C

Reactor pressure: 20 Bar

%(H₂ + CO) conversion: 50-70%

Feed gas composition:

H₂: ca 50 vol%

CO: ca 25 vol%

Balance: Ar, N₂, CH₄ and/or CO₂

Having applied a reported cobalt based Fischer-Tropsch kinetic equation, such as:

$$r_{\text{FT}} = (k_{\text{FT}} P_{\text{H}_2} P_{\text{CO}}) / (1 + K P_{\text{CO}})^2$$

the Arrhenius derived pre-exponential factor of k_{FT} was estimated for each of the reported runs. By defining the relative intrinsic Fischer-Tropsch activity as (pre-exponential factor of catalyst X after reduction test)/(pre-exponential factor of the baseline catalyst B), where X is catalyst A or B, the intrinsic Fischer-Tropsch activities of the cobalt catalysts could be compared. The relative intrinsic Fischer-Tropsch activity is determined after 15 hours on stream (Table 1). It is clear that support modification did not influence the intrinsic Fischer-Tropsch performance characteristics

when compared to the pure alumina supported cobalt catalyst, Catalyst B.

Table 1: Laboratory CSTR Fischer-Tropsch synthesis performance comparison between catalysts prepared on a pure alumina catalyst support (catalyst B) and a Siralox 1.5 successful catalyst support (catalyst A).

	Catalyst A	Catalyst B
Run Number	163F	130S
<u>Synthesis conditions:</u>		
Calcined catalyst mass (g)	20.5	20.6
Reactor temp (°C)	219.3	221.0
Reactor pressure (bar)	20.0	20.0
Time on stream (h)	15.5	15.0
<u>Feed gas composition:</u>		
H ₂ (vol%)	53.2	52.2
CO (vol%)	27.2	26.4
(Balance = Ar, CH ₄ + CO ₂)		
Syngas (H ₂ + CO) space velocity (m _{in} /(kg _{cat} hr))	3.8	3.0
<u>Reactor partial pressures (bar)</u>		
H ₂	5.7	4.5
CO	3.1	2.5
H ₂ O	4.2	4.8
CO ₂	0.2	0.3
<u>Synthesis performance</u>		
Conversion: %syngas	60.1	68.3
Relative intrinsic FT activity	1.1	1.0
%CO of total amount of CO converted to CO ₂	1.5	3.1
%C-atom CH ₄ selectivity	4.0	4.3

DATED THIS 27TH DAY OF JULY 2001.


ADAMS & ADAMS
APPLICANTS PATENT ATTORNEYS

